Intriguing Aspects of of Oxygen Evolution Electrocatalyst Dissolution: Towards Stability Descriptors

Intrigantni aspekti rastvaranja elektrokatalizatora za izdvajanje kiseonika: korak prema deskriptorima stabilnosti

Aleksandar R. Zeradjanin*

Max Planck Institute for Chemical Energy Conversion, Scientific Infrastructure – Electrochemistry Stiftstrasse 34-36, 45470 Mülheim an der Ruhr, Germany

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**aleksandar.zeradjanin@cec.mpg.de*

Abstract

Widespread deployment of sustainable energy technologies is facing limitations due to relatively low efficiency of key energy conversion processes:conversion of renewable energy to electricity, conversion of renewable electricity to chemical energy as well as re-conversion of chemical energy to electricity. One of the essential technologies to convert renewable electricity to chemical energy is water electrolysis. Despite being a topic of investigation for decades, water electrolysis still conceals too many unknowns related to reaction mechanism. That could be the main underlying reason for too many obstacles on the pathway to enhance water electrolysis efficiency. Conversion process is based on two electrocatalytic reactions: facile hydrogen evolution reaction (HER) at the cathode and sluggish oxygen evolution reaction (OER) at the anode. OER is additionally related to severe anode stability issues and therefore it is nowadays more frequently studied. Widely accepted approach to enhance performance of OER anodes is to search for more active electrode materials, while issues related to electrode stability are very often disregarded. Besides gas evolution that has destabilizing effect on electrode surface morphology, very often is lacking significant input to better understanding of intrinsic drivers of electrocatalyst stability. Enhancement of OER anode stability requires existence of straightforward structure-stability relations. In that way, it is possible to tune material properties and interfacial properties of electrode/electrolyte boundary, to achieve long term electrocatalytic performance. Practical precondition for creating link: material properties – interfacial properties – reaction kinetics is to have advanced analytical tools that will allow relevant view on reaction mechanism. Therefore, in this work we propose discussion that will analyse several key aspects of electrode stability in relation to OER electrocatalysis with special focus on what are relevant stability descriptors. Experimental data are gathered using: high-temperature rotating disc electrode (RDE) measurements and scanning flow cell with inductively coupled plasma mass spectrometer (SFC-ICPMS).

Keywords: *oxygen evolution reaction; stability descriptor, activation energy, preexponential factor, compensation effect*

Izvod

Široka primena tehnologija održive energije suočava se sa ograničenjima zbog relativno niske efikasnosti ključnih procesa konverzije energije: pretvaranja obnovljive energije u električnu energiju, pretvaranja obnovljive električne energije u hemijsku energiju, kao i ponovne konverzije hemijske energije u električnu energiju. Jedna od ključnih tehnologija za pretvaranje obnovljive električne energije u hemijsku energiju jeste elektroliza vode. Iako je predmet istraživanja već decenijama, elektroliza vode i dalje skriva previše nepoznanica povezanih sa mehanizmom reakcije. To je verovatno glavni razlog brojnih prepreka na putu ka povećanju efikasnosti elektrolize vode. Proces konverzije zasniva se na dve elektrokatalitičke reakcije: brzoj reakciji izdvajanja vodonika

(HER) na katodi i sporoj reakciji izdvajanja kiseonika (OER) na anodi. OER je dodatno povezana sa problemima stabilnosti anode i zato se danas češće proučava. Opšteprihvaćen pristup unapređenju performansi OER anoda jeste potraga za aktivnijim elektrodnim materijalima, dok se pitanja stabilnosti elektroda vrlo često zanemaruju. Pored izdvajanja gasa, koje destabilizuje morfologiju površine elektrode, često nedostaje značajan doprinos boljem razumevanju unutrašnjih pokretača stabilnosti elektrokatalizatora. Unapređenje stabilnosti OER anode zahteva postojanje jasnih odnosa između strukture elektrode/elektrokatalizatora i stabilnosti. Na taj način moguće je prilagoditi osobine materijala i međupovršinske osobine granice elektroda/elektrolit kako bi se postigle dugotrajne elektrokatalitičke performanse. Praktični preduslov za uspostavljanje veze: osobine materijala – međupovršinske osobine – kinetika reakcije jeste posedovanje naprednih analitičkih metoda koje omogućavaju relevantan uvid u mehanizam reakcije. Stoga u ovom radu predlažemo diskusiju koja će analizirati nekoliko ključnih aspekata stabilnosti elektroda u odnosu na OER elektrokatalizu, sa posebnim fokusom na relevantne deskriptore stabilnosti. Eksperimentalni podaci prikupljeni su korišćenjem merenja rotirajuće disk elektrode na visokim temperaturama (RDE) i protočne ćelije za skeniranje povezane sa masenim spektrometrom sa induktivno spregnutom plazmom (SFC-ICPMS).

Ključne reči: *reakcija izdvajanja kiseonika; deskriptor stabilnosti, energija aktivacije, predeksponencijalni faktor, kompenzacioni efekat*

Introduction

One of the central challenges in modern electrocatalysis is understanding and improving the stability of oxygen evolution reaction (OER) electrocatalysts.[1] While certain progress has been achieved in comprehension and enhancement of electrocatalytic activity, long-term stability remains a major obstacle preventing large-scale implementation of water electrolysis technologies for sustainable hydrogen production.[2] Electrocatalyst degradation, including dissolution phenomena occurring prior and during OER under highly oxidative anodic conditions, is still insufficiently understood despite decades of research. This is of essential importance in acidic environments particularly relevant for proton exchange membrane (PEM) electrolyzers, where only a limited number of noble-metal-based materials such as Ir- and Ru-based oxides exhibit sufficient activity. Unfortunately, these materials also suffer from dissolution and structural degradation during operation.[3]

Generally perception in the community is that electrocatalyst activity and stability are intrinsically interconnected and often inversely related. Highly active electrocatalysts tend to be less stable because the same electronic properties that facilitate oxygen evolution also promote oxidation and dissolution of the electrocatalyst surface. This trade-off, if more universal, will complicate the search for higly active and stable electrocatalysts. It is the fact that trade-off is especially pronounced for Ru-based materials, which display excellent OER activity but poor durability, however Au is example where electrocatalytically less active material exhibits also poor stability. Therefore, meaningful understanding of dissolution processes is necessary and only became possible recently with the development of advanced in situ and in operando characterization techniques. In particular, the coupling of scanning flow cells with inductively coupled plasma mass spectrometry (SFC-ICPMS) represented a major breakthrough. This advanced experimental approach allows real-time monitoring of metal dissolution under dynamic electrochemical conditions with extremely high sensitivity and with possibility to explore multitude of parameters relevant for kinetics of OER and dissolution kinetics. Unlike conventional post-mortem analysis, SFC-ICPMS enables differentiation between transient dissolution events and stationary dissolution processes. Such distinction is essential because catalyst degradation is often highly dynamic and strongly dependent on electrochemical history. Using SFC-ICPMS, it was investigated how numerous experimental variables affect dissolution kinetics laying foundation to understand what material propeorties and interfacial properties could play a role of relevant stability descriptors.

Results and Discussion

1. Place Exchange as Potential-Triggered Transient Process

Numeorus parameters, that are relevant for catalyst stability/dissolution, were investigated in the literature, including: electrode potential, potential scan direction, polarization time, electrolyte composition, pH, dissolved gases, temperature, catalyst loading, particle size, and interparticle distance as well as and electrolyte composition including additives and impurities. Among these factors, applied potential emerges as variables unique for electrocatalytic reactions. Increasing anodic potential generally accelerates oxide formation and promotes dissolution, although the exact mechanism depends strongly on the nature of the electrocatalyst and electrolyte environment. Dissolution rates are often highest during oxidation and reduction transitions rather than under steady-state OER operation what droves particular attention to transient dissolution phenomena occurring during potential cycling.[4] During anodic polarization, surface oxidation can destabilize metal atoms and facilitate their release into the electrolyte. Conversely, cathodic reduction of oxide layers may also trigger dissolution because unstable intermediate oxidation states are formed. This dynamic behavior demonstrates that catalyst degradation cannot be understood solely through equilibrium thermodynamics but instead requires detailed kinetic analysis and dynamic conceptual framework.
On that line of thought important concept is the continuous structural reconstruction of electrocatalyst surfaces prior and during OER. Under operational conditions, many catalysts do not preserve their original structure but instead transform into new oxide or oxyhydroxide phases. Consequently, the catalytically active state often differs substantially from the initially synthesized material. One of the essential reasons for electroctalyst dissolution is mechanism of oxide growth known as place exchange mechanism. It is phenomena where oxygen containing adsorbed species penetrate at the subsurface of oxidized metal pushing out surface metal atoms from equilibrium positions, practically causing lattice distortion making surface metal atoms to be more prone to dissolution. Place exchange mechanism is illustrated in Figure 1.

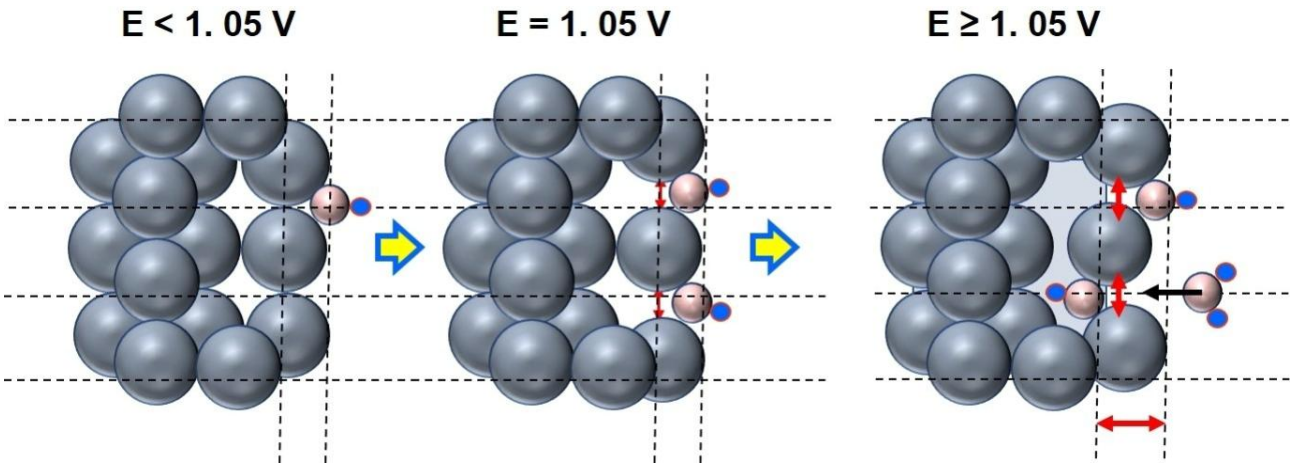

Figure 1. *Illustration of the so called "place-exchange" model of oxide growth that causes lattice instability. Adapted from Ref.4 with permission from Wiley, under the terms and conditions of the Creative Commons Attribution license 4.0 International (2024).*

Namely, when we increse anodic potential, simlutaneously we increase coverage with the adsorbed oxygen-containing species, including signifficant number of M-OH or M-O dipoles in mutual proximity. Formed dipoles exhibit strong electrostatic repulsion and when applied anodic potential is sufficiently high to establish critical coverage at the surface, in order to minimize electrostatic repulsion, oxygen species will migrate at subsurface distorting the lattice by displacing surface metal atoms from their equilibrium positions. Place exchange mechanism as well as other oxide growth

mechanisms, together with phenomena of passivity and transpassivity, represent some of the most important areas o knowledge that will help us reaching of sufficient understanding of electrocatalyst stability.

2. What Could Be Relevant Stability Descritpors?

Taking into consderaiton that coverage with adsorbed oxygen-containing species is driving force for place-exchange while rigidness of the lattice (i.e. that can be described with cohesion energy), is resistive force to place-exchange, we could expect that interplay between M-O (i.e. or M-OH) bond strength and cohesion energy will determine dissolution rate. Noble metals including Pt, Pd, Ir, Ru, Rh, and Au are compared in terms of dissolution behavior. The expectation was that stronger cohesive energy should suppress dissolution because a more strongly bound metal lattice would resist structural distortion. Similarly, stronger metal–oxygen interactions were expected to enhance oxygen adsorption and potentially promote oxide formation and dissolution. However, the experimentally observed trends proved far more complex than anticipated. One of the surprising findings discussed is that dissolution behavior cannot be explained solely by simple correlations with cohesive energy. It seems that dissolution behavior was much more impacted by M-O bond strength as surface property while cohesion energy as bulk property played much less signifficant role.

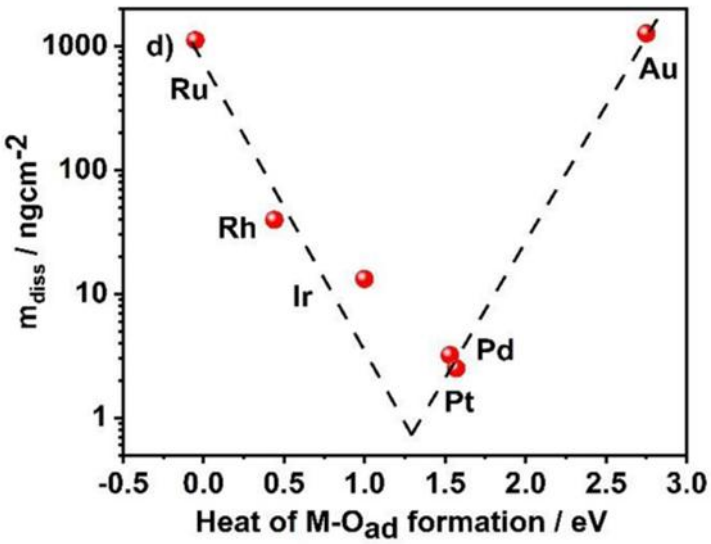

Figure 2. *Correlation of the amount of dissolved metals (Pt, Pd, Ir, Ru, Rh and Au) in 0.1 M $HClO_4$ under galvanostatic polarization at 1 mA cm^{-2} with heat of M−O_{ad} formation. Adapted from Ref.4 with permission from Wiley, under the terms and conditions of the Creative Commons Attribution license 4.0 International (2024).*

From existing results it seems that descriptor of electrocatalyst stability, like in a case of OER activity, could be M-O bond strength. Relation shown in Figure 2 indicates optimal M-O binding that seems to be equivalent to “volcano”-apex in a case of OER acitivty. How close are the value of M-O bond strength at activity maximum and the value of M-O bond strength at stability maximum, still needs to be evalueted experimentally. That information will help us to have better insight how to enhance further activity without comprimising stability.

3. Importance of the Preexponential Frequency Factor in Understanding of Electrocatalyst Stability

High-temperature rotating disk electrode (HT-RDE) experiments reveal that catalyst degradation mechanisms can fundamentally change with temperature. For e.g. Pt dissolution exhibits nearly zero

apparent activation energy yet proceeds very slowly, whereas Ir and Au display much higher dissolution rates despite different activation energies. Furthermore, activation energies often increase alongside dissolution rates, contradicting conventional expectations. These findings indicate that kinetic frequency factors and dynamic surface processes dominate dissolution behavior.

An especially important and intriguing aspect of this work is the discussion of activation energy and the preexponential factor in dissolution kinetics. Experimental results on OER anode dissolution indicate that reducing of activation energy of dissolution process is not necessarily beneficial for enhancement of OER anode stability. Namely, dissolution rates are strongly influenced by preexponential frequency factor. However, because OER electrocatalysts operate under continuously changing surface conditions, both kinetic parameters may vary significantly during operation.

The study demonstrates that dissolution rates can exhibit compensation effects, meaning that variations in activation energy are often accompanied by compensating changes in the preexponential factor. As a result, two catalysts with similar apparent activation energies may display vastly different dissolution behaviors.[5] This finding suggests that simplistic interpretations based solely on thermodynamic descriptors may be insufficient for predicting catalyst durability. Instead, a more comprehensive kinetic framework is required to understand degradation mechanisms. Consequently, stability assessments performed only at room temperature may fail to accurately predict catalyst performance under industrial operating conditions.

Conclusion

Work emphasize that electrocatalyst dissolution occurs on continuously reconstructing surfaces rather than static interfaces. Consequently, conventional kinetic models such as Butler–Volmer equation cannot adequately describe dissolution behavior. Instead, dissolution kinetics is strongly influenced by factors such as proton concentration, active site availability, surface coverage, and dynamic restructuring processes. Therefore, of major importance is to consider how parameters describing interfacial dynamics like collision frequency as well as interplay between activation energy and preexponential factor contribute to reaction kinetics. In that way we could comprehend how activity and stability relate and what are the relevant stability descriptors that can play major role in advanced electrocatalyst design.

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